

Synthesis and Spectral Studies of Alkali Metals with P-Chloroisnitrosoacetophenone (P-Clinap)

P. N. BAGADE¹, R.D. RAUT² and S. Z. JADHAV³

¹Department of Chemistry,
Anand Niketan College, Warora, INDIA.

²Department of Chemistry,
J. B. College of Science, Wardha, INDIA.

³Department of Chemistry,
Institute of Science Nagpur, INDIA.

(Received on: April 18, 2013)

ABSTRACT

Neutral complexes of alkali metals with isonitroso-p-chloroacetophenone have been synthesized and characterized on the basis of elemental analysis, molar conductivities and uv-visible and infrared spectroscopy.

Keywords: Alkali metal complexes, isonitroso-p-chloroacetophenone, Schiff's bases, I.R., U.V. visible spectroscopy.

INTRODUCTION

The ligand p-methyl isonitrosoacetophenone (HIMP) have been used for few analytical applications¹⁻². The structural studies of ligand p-chloroisnitrosoacetophenone (P-CIINAP) has already been studied with transition metals for possible complex formation³. However, structural studies of the complexes of alkali metals with p-chloroisnitrosoacetophenone have not been reported so far. The present paper describes the isolation and characterization of complexes of alkali metals such as Li, Na and K with p-chloroisnitrosoacetophenone

on the basis of elemental analysis and spectral analysis.

EXPERIMENTAL

All the chemicals used were of analytical grade. The ligand p-chloroisnitrosoacetophenone (P-CIINAP) was prepared by the procedure described by Muller and Pechmann⁴. The basic principle underlying this preparation is that of Claisen⁵. It was synthesized by dissolving 11.5 g of sodium in 230 ml of absolute alcohol and to this solution small portions of 58 ml amyl nitrate and then 77 ml of p-chloroacetophenone was added with

constant stirring and cooling in ice bath. The mixture was allowed to stand for three days in a well stoppard bottle in a refrigerator. At the end of this time, the yellowish white sodium salt was obtained. It was filtered and dried in air. The dried sodium salt was dissolved in minimum quantity of ice cooled water and treated with equal volume of water-ethanol mixture. Precipitated p-chloroisoinitrosoacetophenone was then filtered through suction and dried in vacuum. The crude product was recrystallized from benzene. Its melting point was found to be 157⁰ C.

PROCEDURE FOR PREPARATION OF COMPLEXES OF LITHIUM, SODIUM AND POTASSIUM

Preliminary experiments showed that all the complexes could be prepared by the same general procedure by mixing the saturated alcoholic solutions of alkali metal hydroxides and HClINAP.

A saturated 0.01 molar solutions of alkali metal hydroxides in absolute alcohol was added with constant stirring to a saturated 0.02 molar solution of HClINAP in absolute alcohol. Crystalline compounds formed after standing for some time were filtered, washed with alcohol and dried at 110⁰ C.

During isolation of the compounds it was observed that, the complex of potassium was precipitated immediately after mixing of alcoholic solutions of the reactants. The complex of sodium required nearly half an hour after standing for precipitation and the complex of lithium required nearly two hours for the precipitation.

RESULT AND DISCUSSION

Analytical data (table 1) reveals that the complexes which are isolated have the compositions Li(ClINAP)₂, Na(ClINAP)₂ and K(ClINAP)₂. All these compounds are genuine complexes and not stoichiometric mixtures. It is also cleared from the fact their decomposition temperatures were much higher (202⁰ C -248⁰ C) than the melting point of the ligand (157⁰ C)

Conductivity Measurements

Molar conductivities of the complexes of Li, Na and K in acetone are found to be 6,18 and 41 mhos cm² respectively at 10⁻³ M. These values are very low as compared to the value,150 for 1:1 electrolyte in acetone⁶. The values 1.6,41 and 73 mhos cm² respectively at 10⁻⁴ M in acetone suggest that Li complexes as almost non-ionic, but Na and K complexes have partial ionic character.

Electronic Spectra

Electronic spectra of the metal complexes and the ligand (table 2) show internal $\pi \rightarrow \pi^*$ transition of the ligand at 250 nm and 310 nm. The band observed in the range 365-400 nm are due to the charge transfer transition.

I.R.Spectra

In the infra-red spectrum of the ligand in KBr pellet, a broad band is observed in the range 3250-2840 cm⁻¹ due to hydrogen bonded OH of =NOH. Weak broad bands which appear in the Li, Na and K complexes at around 3150,2400 and 2300

cm^{-1} respectively are attributed to the hydrogen bonded OH of the =NOH of one of the ligand molecules. This order of these bands represent that the hydrogen bonding in complexes increase from lithium to potassium. It may be concluded that hydrogen bonding is one of the structures forming features of the alkali metals complexes of the type ML.HL⁷. The increase in decomposition temp. of complexes from Lithium to Potassium (table 1) also confirms the increasing hydrogen bond strength.

The strong absorption at 1705 cm^{-1} is assigned to C=O of the pyrazolone in the spectrum of ligand. Two peaks at 1690 and 1630 cm^{-1} are found in the Li complex. Na and K complexes show two peaks at 1705 and 1600 cm^{-1} . This indicates that perturbation of one of the C=O is less as compared to the other in the Li complex and in the Na and K complexes one is almost unperturbed and the other is perturbed. The strong absorption band at 1050 cm^{-1} in the ligand is assigned to poor N-O stretching frequency. Li complex shows it at 1030 cm^{-1} due to the bonding of the metal ions through O of N-O. These peaks could be due to two

unequally N-bonded N-O groups or they could be assigned to the coupled vibrations of N-bonded N-O⁸⁻⁹. Sodium and potassium complexes show two new bands at 1260 and 1150 cm^{-1} due to N-bonded N → O.

Appearance of new distinct sharp 5-6 peaks in the alkali metal complexes in the range $670-300\text{ cm}^{-1}$ due to the presence of M-N and M-O stretches (table 3) strongly supports the coordination of the ligands to the metal ions.

In the present study, I.R. spectra reveal the presence of strong hydrogen bonding. Further they indicate that Li attached to the ligand through the oxygen of N-O group and oxygen of the C=O. The ligand molecules in the Na and K complexes are attached to the metal ion through the nitrogen of oxime groups. Their structures can be represented as shown in fig.1. From the partial ionic nature of Sodium and Potassium complexes, they can be considered to have polymeric structures similar to that of sodium hydrogen bis and potassium hydrogen bisisonitrosoacetophenone¹⁰.

Table-1 Analytical data of the metal complexes

Compound	% C	% H	% N	% M	m.p.@ ($^{\circ}\text{C}$)
(ClINAP) ₂ Li	51.80	2.71	7.58	1.91	201
	(51.62)	(2.69)	(7.53)	(1.87)	
(ClINAP) ₂ Na	49.51	2.61	7.25	5.98	212
	(49.49)	(2.58)	(7.22)	(5.93)	
(ClINAP) ₂ K	47.55	2.54	6.98	9.75	249
	(47.52)	(2.48)	(6.93)	(9.65)	

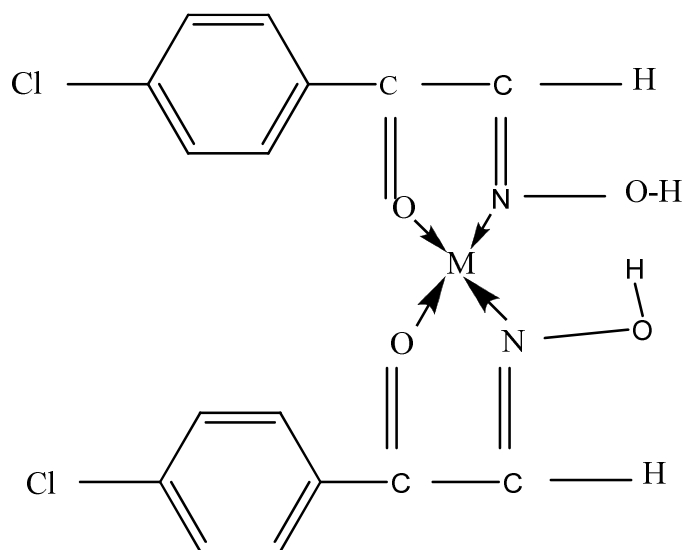
*Calculated values are given in parenthesis @ decomposition temperature

Table 2- Electronic spectral data of the metal complexes in methanol

Compound	max(nm)	max	Tentative assignment
p-ClINAP	250	32,000	$\pi \rightarrow \pi^*$
	310	29,500	$\pi \rightarrow \pi^*$
	390	5,950	charge transfer
(ClINAP) ₂ Li	250	58,000	$\pi \rightarrow \pi^*$
	300	17,500	$\pi \rightarrow \pi^*$
	400	1,300	charge transfer
(ClINAP) ₂ Na	250	45,500	$\pi \rightarrow \pi^*$
	310	22,600	$\pi \rightarrow \pi^*$
	365	3,500	charge transfer
(ClINAP) ₂ K	250	50,500	$\pi \rightarrow \pi^*$
	310	19,000	$\pi \rightarrow \pi^*$
	365	3,400	charge transfer

STRUCTURE AND BONDING

On the basis of elemental analysis, molar conductance measurement, IR and UV-VIS spectral studies, the probable structures of the complexes can be produced schematically as fig.1

**Fig.1 : M = alkali metals Li, Na and K**

REFERENCES

1. Barhate V D, Patil M R, *Curr. Sci. (India)*, 58,291(1989).
2. Patel N J and Halder B C, *J. Inorg. Nucl. Chem.*, 29, 1037(1967).
3. Raut R D *et al.*, *J. Chem. Pharm. Res.*, 3(6), 195-199 (2011).
4. Muller H and Pechmann V, *J. Chem. Soc.*, 51,(1980).
5. Victor Meyer, Zubin J., *Ber*, 11, 695 (1878).
6. Lee A J, *J. Chem. Soc. A* 2007 (1971).
7. Banerjee A K *et al.*, *J. Indian Chem. Soc.*, 56, 442 (1979).
8. Bline R and Hadzi D, *J. Chem. Soc.* 4356, (1958).
9. Iyengar R R and Patel C C, *Indian J. Chem.* 16 A,846, (1978).
10. Poonia N S and Mary R Truter *J. Chem. Soc. Dalton*, 1791 (1992).